

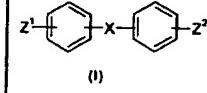
DE 10023441

2002-089784/12 BASF AG 2001.01.17 2001-1(X)1939(+2000DE-1023471) (2001.11.15) C07F 9/00	E19 BADI 2000.05.12 WO 200185739-A1	E(5-G <sub>2</sub> , 5-G <sub>8</sub> , 5-G9B, 5-H, 5-J, 5-M, 5-N, 10-DIC) N(2-E, 2-E2, 2-F2, 5-E1, 7-D2A)
Hydroformylation of olefin for production of aldehyde, using a Sub-Group VIII metal complex catalyst with a special ligand in which two phosphorus-substituted phenyl groups are attached to a non-aromatic cyclic group (Ger)		
C2002-027654 N(AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW) R(AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU MC MW MZ NL OA PT SD SE SL SZ TR TZ UG ZW)		
Addnl. Data: AHLERS W, PACIELLO R, ROEPER M, HOFMANN P, TENSFELDT M, GOETHLICH A 2001.05.11 2001WO-EP05407, 2001.01.17 2001DE-1001939		
<b>NOVELTY</b>		

Hydroformylation of olefins is carried out in presence of a catalyst comprising a Sub-Group VIII metal complex with a ligand in which two phenyl groups substituted with phosphorus-, arsenic- or antimony-containing residues are attached to a non-aromatic, 3- to 8-membered, carbo- or hetero-cyclic, divalent bridging group.

#### DETAILED DESCRIPTION

A method for the hydroformylation of compounds with ethylenic double bond(s) by reaction with hydrogen and carbon monoxide in presence of a hydroformylation catalyst, in which the catalyst comprises complex(es) of Sub-Group VIII metal(s) with ligand(s) of formula (I).



X = a non-aromatic, 3- to 8-membered, carbo- or hetero-cyclic divalent bridging group with 1, 2 or 3 double bonds and 1, 2, 3 or 4 single bonds.

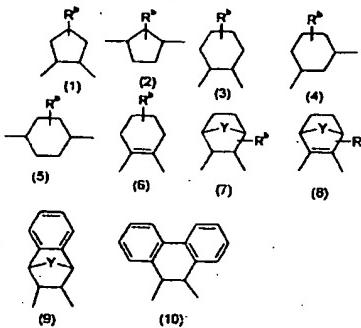
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<p>4 substituents selected from alkyl, cycloalkyl, aryl, heteroaryl, alkoxy, acyl, carboxyl, alkoxycarbonyl, hydroxy, nitro, cyano, trifluoromethyl, oxo (or their ketals) or -NE<sup>1</sup>E<sup>2</sup>, and X may be part of a condensed ring system with 1, 2 or 3 other rings (optionally with 1, 2 or 3 substituents as above), and X itself may be bridged by -O-, -S-, -N(Ra)- or another bridging group; E<sup>1</sup>, E<sup>2</sup> = alkyl, cycloalkyl or aryl; Ra = H, alkyl, cycloalkyl or aryl; Z<sup>1</sup>, Z<sup>2</sup> = a phosphorus-, arsenic- or antimony-containing residue. An INDEPENDENT CLAIM is also included for a catalyst as above.</p> <p><b>USE</b> For the hydroformylation of ethylenically unsaturated compounds, i.e. for the production of aldehydes from olefins.</p> <p><b>ADVANTAGE</b> Enables the hydroformylation of <math>\alpha</math>-olefins with high selectivity for the formation of <math>\alpha</math>-aldehydes or alcohols and the hydroformylation of linear internal olefins with high regioselectivity in favor of terminal aldehydes. The catalysts used are mostly new Sub-Group VIII metal-phosphine complexes with high stability under hydroformylation conditions.</p>	<p><b>EXAMPLE</b> Trans-1,2-bis-[o-(diphenylphosphino)-phenyl]-cyclopentane (ligand II) was obtained from methyl o-chloro-trans-cinnamate by (a) reaction with sodium sand in THF to give 2-carbomethoxy-3,4-bis(o-chlorophenyl)-cyclopentanone, which was separated into the cis and trans isomers (34.6% and 16.3% respectively) by crystallisation, chromatography and recrystallization, (b) hydrolysis of the trans-ester with 48% hydrobromic acid and decarboxylation at 130 °C to give trans-3,4-bis(o-chlorophenyl)-cyclopentanone (80.5% yield after flash chromatography), (c) reduction to the corresponding cyclopentane derivative by reaction with hydrazine hydrate and potassium hydroxide in triethylene glycol at 160 °C (83.5% yield) and (d) reaction of the chloro compound (3.54 mmols) with lithium in THF (21 hours at -78 °C) followed by filtration and reaction with 7.43 mmols diphenylchlorophosphane (at -50 °C and -30 °C and then overnight at room temperature) to give ligand (II) in 38% yield (after recrystallization from acetone). A mixture of 2.1 mg rhodium bis-carbonyl-acetylacetone, 17.8 mg ligand (II), 6 g 1-octene and 6 g toluene was reacted with synthesis gas (CO/H<sub>2</sub> ratio = 1:1) for 4 hours at 90 °C and 10 bar. GC analysis of the product mixture showed a</p>
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conversion of 99%, with a selectivity of 97% for $\alpha$ -isomers (n-aldehyde and iso-aldehyde).	
<b>DEFINITIONS</b> Preferred Definitions:	<p>alkyl, cycloalkyl, heterocycloalkyl, aryl heteroaryl, COOR<sub>f</sub>, COO<sup>M</sup>, SO<sub>3</sub>R<sub>f</sub>, SO<sub>3</sub><sup>M</sup>, NE<sup>1</sup>E<sup>2</sup>, alkylene-NE<sup>3</sup>E<sup>4</sup>, R<sub>f</sub>, E<sup>3</sup>, E<sup>4</sup>, E<sup>5</sup> = H, alkyl, cycloalkyl or aryl; R<sub>g</sub> = H, methyl or ethyl; M = a cation; X = an anion; or a group of formula (II.1)-(II.3), y = 1-120, or R<sup>1</sup> and R<sup>2</sup> plus the P atom and optionally the attached O atom(s) may form a 5- to 8-membered heterocycle (optionally annelated with 1, 2 or 3 cycloalkyl, heterocycloalkyl, aryl or heteroaryl residues and optionally substituted on each ring with 1, 2, 3 or 4 groups as above), A<sup>1</sup>, A<sup>2</sup> = B, N, P or CR<sup>5</sup>, R<sup>3</sup> = H, alkyl, cycloalkyl or aryl; D<sup>1</sup> = a single bond or 1-3C alkylene (optionally with 1 double bond and 1 or 2 substituents selected from alkyl, cycloalkyl, aryl, alkoxy, acyl, carboxyl, alkoxycarbonyl, OH, nitro, CN, CF<sub>3</sub>, oxo</p>
Z <sup>1</sup> , Z <sup>2</sup> = PR <sup>1</sup> R <sup>2</sup> , OPR <sup>1</sup> R <sup>2</sup> , P(OR <sup>1</sup> )R <sup>2</sup> , P(OR <sup>1</sup> )(OR <sup>2</sup> ), OP(OR <sup>1</sup> )R <sup>2</sup> or OP(OR <sup>1</sup> )(OR <sup>2</sup> ); R <sup>1</sup> , R <sup>2</sup> = alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl (optionally substituted with 1, 2 or 3 groups selected from	WO 200185739-A+/2

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(or ketals) or  $\text{NE}^1\text{E}^2$ ,  
 $\text{D}^2 = 3\text{-}6\text{C alkylene}$  (optionally with 1, 2 or 3 double bonds and 1, 2 or 3 substituents as for  $\text{D}'$ , and  $\text{D}^2$  in (II.1) and (II.3) may be bridged by a group  $\text{Y}$ ;  
 $\text{Y} = \text{O, S, CRxRy}$  or a group of formula (III.1)-(III.4);  
 $\text{Rx, Ry} = \text{H, alkyl, cycloalkyl, aryl or heteroaryl};$   
 $\text{X} = \text{one of the following groups (1-10);}$   
 $\text{Rb} = \text{alkyl, cycloalkyl, aryl, alkoxy, acyl, carboxyl, alkoxycarbonyl, OH, nitro, CN, CF}_3$ , oxo (or ketals) or  $\text{NE}^1\text{E}^2$ .

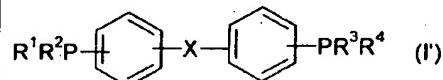


#### TECHNOLOGY FOCUS

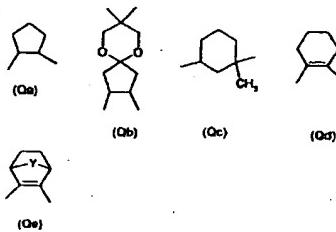
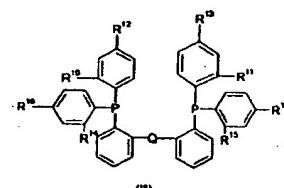
Organic Chemistry - Preferred Ligand: The ligand is of formula (I') or (I'').

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$\text{R}^1\text{-R}^4 = \text{alkyl, cycloalkyl, aryl or heteroaryl}$  (the last 3 types optionally substituted with 1, 2 or 3 alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxycarbonyl or  $-\text{NE}^3\text{E}^4$  groups;  
 $\text{E}^3, \text{E}^4 = \text{E}^1$  and  $\text{E}^2$ .



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$\text{Q} = \text{a group of formula (Qa)-(Qe)}$  (ligands (Ia)-(Ie) respectively);  
 $\text{R}^{10}, \text{R}^{11} = \text{H}$  in (Ia) or methyl in the other formulae;  
 $\text{R}^{12}, \text{R}^{13} = \text{H}$  in (Ia)-(Ic) and methyl in the others;  
 $\text{R}^{14}, \text{R}^{15} = \text{H}$  in (Ia), (Ib) and (Id) and methyl in the others;  
 $\text{R}^{16}, \text{R}^{17} = \text{H}$  in (Ia)-(Id) and methyl in (Ie);  
 $\text{Y} = \text{O, S, CH}_2$  or a group of formula (III.1)-(III.4);  
 $\text{R}^6\text{-R}^9 = \text{H, alkyl, cycloalkyl, aryl, alkoxy, halogen, SO}_3\text{H, sulfonate, NE}^1\text{E}^2$ , alkylene- $\text{NE}^1\text{E}^2$ ,  $\text{CF}_3$ , nitro, alkoxycarbonyl, carboxyl or CN.

Other ligand(s) which may be present include halides, amines, carboxylates, acetylacetone, aryl- or alkyl-sulfonates, hydride, carbon monoxide, olefins, dienes, cyclo-olefins, nitriles, N-heterocycles, aromatics, hetero-aromatics, ethers,  $\text{PF}_6^-$ , phospholes, phosphabzenes and mono-, bi- or multi-dentate phosphine, phosphinite, phosphonite, phosphoramidite and phosphite ligands.  
Preferred Compound: Compound of formula (I) has at least two optionally substituted hetero-atoms (O, S or NRA) directly attached to the P, As or Sb atoms in  $\text{Z}^1$  and  $\text{Z}^2$ , not including compounds in which  $\text{X} = \text{cyclopentylene}$ ,  $\text{Z}^1$  and  $\text{Z}^2 = \text{PR}^1\text{R}^2$  and  $\text{R}^1, \text{R}^2 = \text{phenyl or naphthyl}$  with the phenyl residues optionally substituted with 1, 2 or 3 halogen, alkyl or alkoxy groups. Compound (I) is of formula (I'), not including those in which  $\text{X} = \text{cyclopentylene}$  and  $\text{R}^1\text{-R}^4 = \text{optionally}$

substituted phenyl or naphthyl.  
Inorganic Chemistry - Preferred Catalyst: The catalyst metal is cobalt, ruthenium, iridium, rhodium, nickel, palladium or platinum. (65pp1712DwgNo.0/0)

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**Hydroformylation of olefin for production of aldehyde, using a Sub-Group VIII metal complex catalyst with a special ligand in which two phosphorus-substituted phenyl groups are attached to a non-aromatic cyclic group**

**Patent number:** DE10023471  
**Publication date:** 2001-11-15  
**Inventor:** AHLERS WOLFGANG (DE); PACIELLO ROCCO (DE); ROEPPER MICHAEL (DE); HOFMANN PETER (DE); TENSFELDT MARKUS (DE); GOETHLICH ALEXANDER (DE)  
**Applicant:** BASF AG (DE)  
**Classification:**  
- **international:** C07F15/00; C07F15/06; C07F15/00; (IPC1-7): C07C45/50; B01J31/12  
- **european:** C07F15/00N3B; C07F15/00N4B; C07F15/00N5B; C07F15/00N6B; C07F15/00N7B; C07F15/06B  
**Application number:** DE20001023471 20000512  
**Priority number(s):** DE20001023471 20000512

[Report a data error here](#)**Abstract of DE10023471**

Hydroformylation of olefins is carried out in presence of a catalyst comprising a Sub-Group VIII metal complex with a ligand in which two phenyl groups substituted with phosphorus-, arsenic- or antimony-containing residues are attached to a non-aromatic, 3- to 8-membered, carbo- or hetero-cyclic, divalent bridging group. A method for the hydroformylation of compounds with ethylenic double bond(s) by reaction with hydrogen and carbon monoxide in presence of a hydroformylation catalyst, in which the catalyst comprises complex(es) of Sub-Group VIII metal(s) with ligand(s) of formula (I). X = a non-aromatic, 3- to 8-membered, carbo- or hetero-cyclic divalent bridging group with 1, 2 or 3 double bonds and 1, 2, 3 or 4 substituents selected from alkyl, cycloalkyl, aryl, heteroaryl, alkoxy, acyl, carboxyl, alkoxy carbonyl, hydroxy, nitro, cyano, trifluoromethyl, oxo (or their ketals) or -NE<1>E<2>, and X may be part of a condensed ring system with 1, 2 or 3 other rings (optionally with 1, 2 or 3 substituents as above), and X itself may be bridged by -O-, -S-, -N(Ra)- or another bridging group; E<1>, E<2> = alkyl, cycloalkyl or aryl; Ra = H, alkyl, cycloalkyl or aryl; Z<1>, Z<2> = a phosphorus-, arsenic- or antimony-containing residue. An Independent claim is also included for a catalyst as above.

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